The University of Chicago

I. THE STRUCTURE OF ELECTRONIC BANDS OF POLYATOMIC MOLECULES

II. VIBRATIONAL ANALYSIS OF THE ABSORPTION SYSTEM OF SULPHUR DIOXIDE AT λ3400-2600

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY

DEPARTMENT OF PHYSICS

1941

By

NICHOLAS C. METROPOLIS

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The Structure of Electronic Bands of Polyatomic Molecules

I. Prolate Approximation for XY_2 Molecules

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A study has been made of the rotational structure of electronic bands of polyatomic molecules whose moments of inertia are related approximately like those of a symmetrical top, with the object of facilitating the interpretation of observed (resolved or unresolved) structures. The present discussion concerns non-linear XY_2 molecules, but it is also valid for all polyatomic molecules that come approximately under the prolate symmetrical top classification. The four characteristic cases of changes in dimensions during the electronic transition are considered and yield four typically different band structures. The variation in band structure with bond distance and apex angle is worked out in detail for SO_2 molecules and theoretical quantitative diagrams of band structures are given, for a temperature of 200°K. The intensity distributions shown in these diagrams are valid (for some adjusted temperature) for any polyatomic molecules in which the moments of inertia of the ground state have the same ratio as those in SO_2. If, in addition, the same is true of the moments of inertia in the upper states, then the entire band structure is identical at some adjusted scale. The correlation between rotational structure and vibrational intensity distribution is worked out, from which conclusions about the changes in dimensions of the XY_2 molecule in the transition can be made. It is shown how a qualitative examination of the observed (resolved or unresolved) rotational structure may guide or confirm the associated vibrational analysis. Finally a comparison with the available data on SO_2 and ClO_2 is made.

INTRODUCTION

THE problem of analyzing electronic bands of non-linear molecules is, at best, a complicated one. One reason for this is the fact that the expressions for the rotational energy levels of non-linear, as compared to linear, molecules contain a second rotational quantum number. As is well known, the expressions are those derived by the quantum mechanics for a freely rotating top, either symmetrical or asymmetrical.[1] The most suitable approximations will depend, for a particular molecule, upon the relative values of its three principal moments of inertia. Following the notation used by Mulliken,[2] let these be I_a, I_b, I_c with $I_a \leq I_b \leq I_c$. For planar molecules, and in particular non-linear XY_2 molecules, $I_c = I_a + I_b$, so that, in general, non-linear triatomic molecules are of the asymmetrical top type. However, there is a particular value, say $2\alpha_{ob}$, of the YXY apex angle 2α, dependent only on the masses of the X and Y atoms, such that

$$I_a = I_b = \tfrac{1}{2} I_c$$

holds, yielding an oblate-symmetrical top. Now

[1] D. M. Dennison, Phys. Rev. **28**, 318 (1926); F. Hund, Zeits. f. Physik **43**, 805 (1927); H. A. Kramers and G. P. Ittmann, Zeits. f. Physik **58**, 217 (1929); O. B. Klein, Zeits. f. Physik **58**, 730 (1929); S. C. Wang, Phys. Rev. **34**, 243 (1929); D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931); W. H. Shaffer and H. H. Nielsen, Phys. Rev. **56**, 188 (1939).

[2] A complete discussion of top and species classifications of non-linear triatomic molecules has been given recently by R. S. Mulliken, Phys. Rev. **59**, 873 (1941).

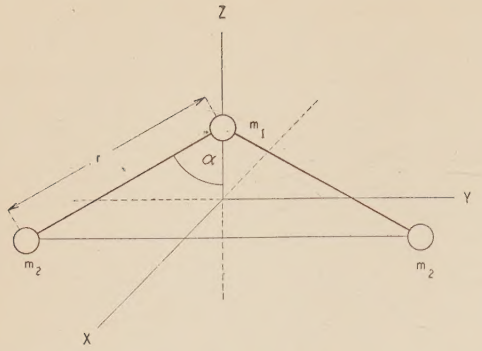

FIG. 1. XY_2 molecule.

then, if the actual value of 2α is near to $2\alpha_{ob}$, the molecule, strictly speaking, rotates like an asymmetrical top; nevertheless its wave functions and energy level patterns approximate those of the oblate-symmetrical top (see Fig. 4 of reference 2), and accordingly one may speak of the molecule as belonging to the near-oblate top classification. For 2α sufficiently far from $2\alpha_{ob}$, prolate top approximations to the wave functions and energy levels become valid. The acute near-prolate top or the obtuse near-prolate top case[2] obtains according as $\alpha \ll \alpha_{ob}$ or $\alpha \gg \alpha_{ob}$. For intermediate values of α, both symmetrical top approximations are poor.

The present discussion primarily concerns electronic spectra of non-linear XY_2 molecules in which the molecule in both upper and lower states belongs to the near-prolate top classification. Since, almost exclusively, the obtuse near-prolate case occurs in practice, the following discussion, for the most part, refers to this case. The changes necessary to cover the acute near-prolate case are quite simple and are given in the footnotes. A study of molecules which are of the near-oblate top classification in both states and of the mixed case where the top classification is different in the two states is in preparation.

For a particular XY_2 molecule, the values of the rotational constants [see Eqs. (2) below] depend, of course, on the values of the XY bond distance and of the apex angle. In an electronic transition the bond distance and angle will, in general, change. Two questions immediately arise: (1) How do the rotational constants depend upon the shape of the molecule? (2) What is the appearance of the resulting band structure for various possibilities as to shapes in upper and lower states? It was these points that had to be considered for SO_2, when the rotational spectrum of the λ3880 system was first photographed. Spectrograms of this system,[3] taken in first and second order of the 30-foot grating spectrograph, exhibited a curious shading toward both shorter and longer wave-lengths. Consideration of the above questions soon showed that an increase in bond distance and in angle could account for the two-sided shading. Because of the rather interesting results obtained, a systematic investigation has been carried through.

Hypothetical band structures for SO_2 have been computed and plotted, with symmetrical top formulas to approximate the rotational levels.[4] Electron diffraction values were used for the dimensions of the ground state and various reasonable assumptions were made about the dimensions in the excited state. Both parallel- and perpendicular-type bands have been considered.

A study of these plots showed that these band structures are examples of four general types whose qualitative aspects depend only on the signs of the changes in dimensions. Furthermore, such band structures are not limited to SO_2 and SO_2-like molecules, but must occur quite generally for XY_2 and other molecules, provided only that the moments of inertia in both states are related approximately like those of prolate symmetrical top.

For XY_2 molecules which satisfy the latter condition, it turns out that a qualitative treatment of the observed (resolved or unresolved) band structures may lead to definite conclusions concerning (1) relative values of bond distances and of angles of the molecule in upper and lower states; (2) direction of quantum-mechanical dipole moment; (3) intensity distribution to be expected in the associated vibrational structure in case the latter has not yet been analyzed: for there exist definite relations, based on the Franck-Condon principle, between the rotational and vibrational structures; or on the other hand,

[3] N. Metropolis and H. Beutler, Phys. Rev. **57**, 1078A (1940).

[4] G. H. Dieke and G. B. Kistiakowsky, Phys. Rev. **45**, 4 (1934), and L. Harris and G. W. King, J. Chem. Phys. **8**, 775 (1940).

a vibrational analysis already made can be confirmed.

Rotational Structures and Band Shading

In infra-red band spectra of diatomic molecules, the equilibrium nuclear separation, r_e, remains nearly constant in transitions to higher vibrational and rotational states. As a result, each band appears as a series of nearly evenly spaced lines on both sides of the origin. In rare cases, heads may be formed. In marked contrast, electronic bands are transitions in which the equilibrium nuclear separations are usually different in the two states, so that heads are formed. For diatomic molecules, it is well known that the bands degrade toward the ultraviolet or the red according as $r_e' < r_e''$ or $r_e' > r_e''$.

In polyatomic molecules, there is greater complexity in band structures, together with a greater variety of possibilities in band shading. To a good approximation, the rotational terms of an asymmetrical top molecule, if two moments of inertia are even roughly equal and differ markedly from the third (unique) moment, may be written

$$F = BJ(J+1) + CK^2 \tag{1}$$

where, for the near-prolate case,[5]

$$\begin{aligned} B &= (h/8\pi^2 c)\tfrac{1}{2}(1/I_b + 1/I_c); \\ C &= (h/8\pi^2 c)[1/I_a - \tfrac{1}{2}(1/I_b + 1/I_c)]. \end{aligned} \tag{2}$$

J is the total angular momentum quantum number, and K is the approximately valid quantum number associated with the component of the total angular momentum along the axis of the unique moment of inertia (quasi-symmetrical-top axis). Necessarily $J \geq K$.

The rotational levels of the normal and excited states in a spectroscopic transition are given by Eq. (1) with B', C' for the upper levels and B'', C'' for the lower. The allowed transitions[1] are given by $\Delta J = 0, +1, -1$, which correspond respectively to the Q, R and P branches of the "J structure," and by $\Delta K = 0, \pm 1$, which correspond to the q, r and p branches of the "K structure." The two cases, $\Delta K = 0$ and $|\Delta K| = 1$, which usually occur only in separate vibrational or electronic transitions, are referred to as "parallel-type" and "perpendicular-type" transitions because of the orientation of the quantum-mechanical dipole moment parallel or perpendicular to the unique axis of the symmetrical or quasi-symmetrical top.

It is convenient to write

$$\nu_{KJ} = \nu_0 + \nu_K + \nu_J, \tag{3}$$

where ν_0 is the band origin, and where

$$\nu_K = C'K'^2 - C''K''^2, \tag{4}$$

giving the K structure, and

$$\nu_J = B'J'(J'+1) - B''J''(J''+1), \tag{5}$$

giving the J structure. Usually the distance between lines is much smaller for one structure than for the other. This fact makes it convenient

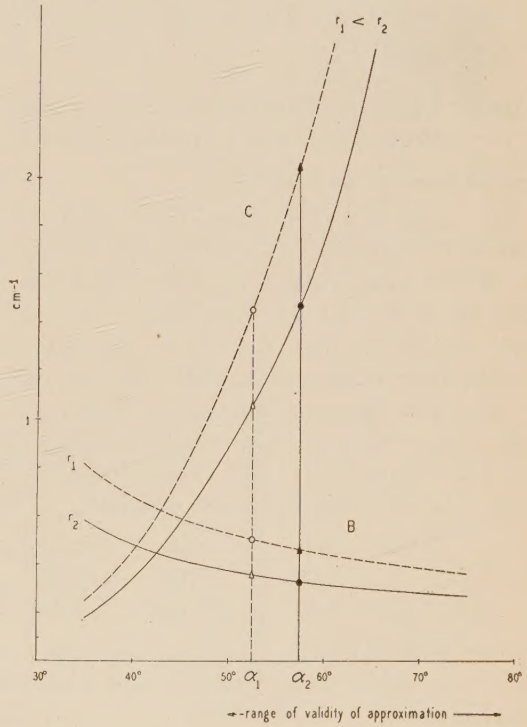

FIG. 2. Graphs showing the behavior of the rotational constants B and C of Eq. (1) as functions of the half-angle α at the apex for *constant bond distance*. The solid curves are for a state having a bond distance r_2, the dashed curves are for a state having $r_1 = 0.85 r_2$. Other r_1/r_2 ratios would give similar curves. α_1 and α_2 are two sample values of α. The scale for ordinates applies to SO_2; the value of r_2 is 1.43A, the experimental value for the normal state. For any other XY_2 molecule belonging to the obtuse near-prolate top classification, the curves have approximately the same shape. Although no sharply defined limit exists for the range of validity, this extends approximately to 50°. As α approaches 90°, C tends toward infinity, while B approaches $h/8\pi^2 c(2m_2 r^2)$; all C curves cross the α-axis at $\alpha = \tan^{-1}[\sqrt{2}(1+2m_2/m_1)]^{-\frac{1}{2}}$.

[5] It is easily seen that for XY_2 molecules $I_b = 2m_2 r^2 \sin^2\alpha$, and $I_a = (2m_1 m_2/m_1 + 2m_2) r^2 \cos^2\alpha$.

to regard the frequencies of the coarser structure as giving the positions of sub-band origins, e.g., the frequencies $\nu_0+\nu_K$ of Eq. (4) if the K structure is the coarser, as for molecules like SO_2.[6] The sub-bands themselves are made up of sets of lines constituting fine structure, the frequencies being given by ν_J of Eq. (5).

In infra-red studies, the coefficients B' and B'' are nearly equal in the two states, just as in the diatomic case. Similarly C' and C'' are nearly equal. Hence the series of lines and sub-bands forming the band structure due to $|\Delta K|=1$ or $|\Delta J|=1$ exhibit slow convergence, if any, while series corresponding to $\Delta K=0$ or $\Delta J=0$ exhibit little if any *divergence*. On the other hand, the values of B and C may be quite different in the two states if a transition involves a change in the electronic state. This is the case in which we are interested.

Dependence of Rotational Coefficients upon Bond Distance and Apex Angle

Special cases to be treated

The available experimental data show that a number of non-linear XY_2 molecules belong to the obtuse near-prolate top type. This follows from the fact that 2α (see Fig. 1) is usually large enough so that $I_c \approx I_b > I_a$. Thus in the normal states of SO_2, NO_2 and ClO_2, the values of 2α from electron diffraction studies and spectroscopic data are approximately 120°, 154° and 122° respectively. For these values of the angles, the following ratios are obtained

	SO_2	NO_2	ClO_2
I_c/I_a	7.00	7.16	7.23
I_c/I_b	1.17	1.16	1.16

(In Fig. 1 for XY_2, the moments of inertia I_c, I_b and I_a are those about the x, y and z axes respectively.)

As an aid to analyzing actual spectra, it is useful to work out the band structures for the four following cases:

$$\begin{aligned} &\text{I.} && \alpha'>\alpha'', && r'=r'' \\ &\text{II.} && \alpha'<\alpha'', && r'=r'' \\ &\text{III.} && \alpha'=\alpha'', && r'>r'' \\ &\text{IV.} && \alpha'=\alpha'', && r'<r''. \end{aligned} \tag{6}$$

Table I. *Character of band structures in four special cases for XY_2 molecules belonging to the obtuse near-prolate top classification.*

	Case	B	C	J Structure Degrades Toward	K Structure Degrades Toward
I	$\alpha'>\alpha'', r'=r''$	$B'<B''$	$C'>C''$	red	violet
II	$\alpha'<\alpha'', r'=r''$	$B'>B''$	$C'<C''$	violet	red
III	$\alpha'=\alpha'', r'>r''$	$B'<B''$	$C'<C''$	red	red
IV	$\alpha'=\alpha'', r'<r''$	$B'>B''$	$C'>C''$	violet	violet

In a discussion of these cases, it is useful to consider Fig. 2. The solid curves show the behavior of B and C [cf. Eq. (2)] for SO_2 as functions of the half-angle at the apex, for a *constant bond distance* $r_2=1.43$A. The dashed curves are similar functions for a bond distance $r_1=0.85r_2$. Curves for other XY_2 molecules are qualitatively the same as these for SO_2; the C curves are always monotonic increasing and the B curves monotonic decreasing functions.[6a] In Fig. 2, α_1 and α_2 are two sample values of α such that $\alpha_1<\alpha_2$.

For cases I and II, where only the angle changes in the transition, the behavior of B and C is immediately apparent; if α increases in an absorption transition (suppose $\alpha''=\alpha_1$, $\alpha'=\alpha_2$) C increases markedly but B decreases slightly, whereas for $\alpha'<\alpha''$, the directions of the changes in B and C are reversed.

For cases III and IV, where only the bond distance changes in the transition, it is easy to show that $B'=[(r''/r')^2]B''$ and $C'=[(r''/r')^2]C''$. Hence a change in bond distance alone increases both B and C if $r'<r''$, decreases both if $r'>r''$. If, for example, in Fig. 2, $\alpha''=\alpha'=\alpha_2$ and $r''=r_2$ and $r'=r_1$, all that is necessary is to move along the vertical from the solid circles to the solid triangles. The foregoing relations are summarized in Table I; the direction toward which each

[6] A convenient qualitative method for comparing the relative coarseness of spacing of J and K structures is the following: (i) For parallel-type bands, the span of, say, the first ten Q lines from the head may be compared with that of the first ten q transitions. (ii) For perpendicular-type transitions, the span of the first ten lines from the head of the J structure (P or R branch) in some strong sub-band may be compared with that of the first ten transitions from the head of the K structure (p or r branch). Using this criterion for case II in SO_2 (see Fig. 4) one finds that the K structure is about five and seven times as coarse as the J structure for the parallel- and perpendicular-types, respectively.

[6a] The corresponding curves for the acute near-prolate top case are approximately those obtained by reflecting the curves in Fig. 2 at $\alpha=45°$. Consequently the present discussion applies to the acute form provided the inequality signs in $\alpha'<\alpha''$ and in $\alpha'>\alpha''$, wherever used, are reversed.

structure degrades in each of the four cases is also indicated.

Characteristic patterns of bands

The four representative cases considered above yield four characteristic band structures.[7] For case I, where $\alpha' > \alpha''$ results in $C' > C''$ and $B' < B''$, the K structure degrades toward the violet, whereas the J structure goes off toward the red. Case II with $\alpha' < \alpha''$ reverses both directions of shading. Cases I and II will thus exhibit a shading of K structure to one side with a superposition of J structure shaded to the other. The band as a whole will not have a

[7] Explicit band formulas for the two types of transitions are as follows. For the perpendicular type ($\Delta K = \pm 1$), the formula [cf. Eq. (3)] may be written

$$\nu = \nu_0 + \tfrac{1}{2}(C' - C'')(C' + C'')k + (C' - C'')k^2 + \begin{cases} (B' + B'')m + (B' - B'')m^2 \\ (B' - B'')J + (B' - B'')J^2 \end{cases}.$$

Here k is a convenient index number with the value $k = K + \frac{1}{2}$ for the r branch and $k = -K + \frac{1}{2}$ for the p branch of the K structure [cf. Eq. (4)]. The bracketed expressions represent ν_J of Eq. (5). The lower expression for ν_J corresponds to the Q branch; in the upper expression, the index number m with $m = J + 1$ gives the R branch, and with $m = -J$ the P branch. For parallel-type transitions, the formula may be written

$$\nu = \nu_0 + (C' - C'')K^2 + \begin{cases} (B' + B'')m + (B' - B'')m^2 \\ (B' - B'')J + (B' - B'')J^2 \end{cases}.$$

In all the foregoing formulas, K means K'', J means J''.

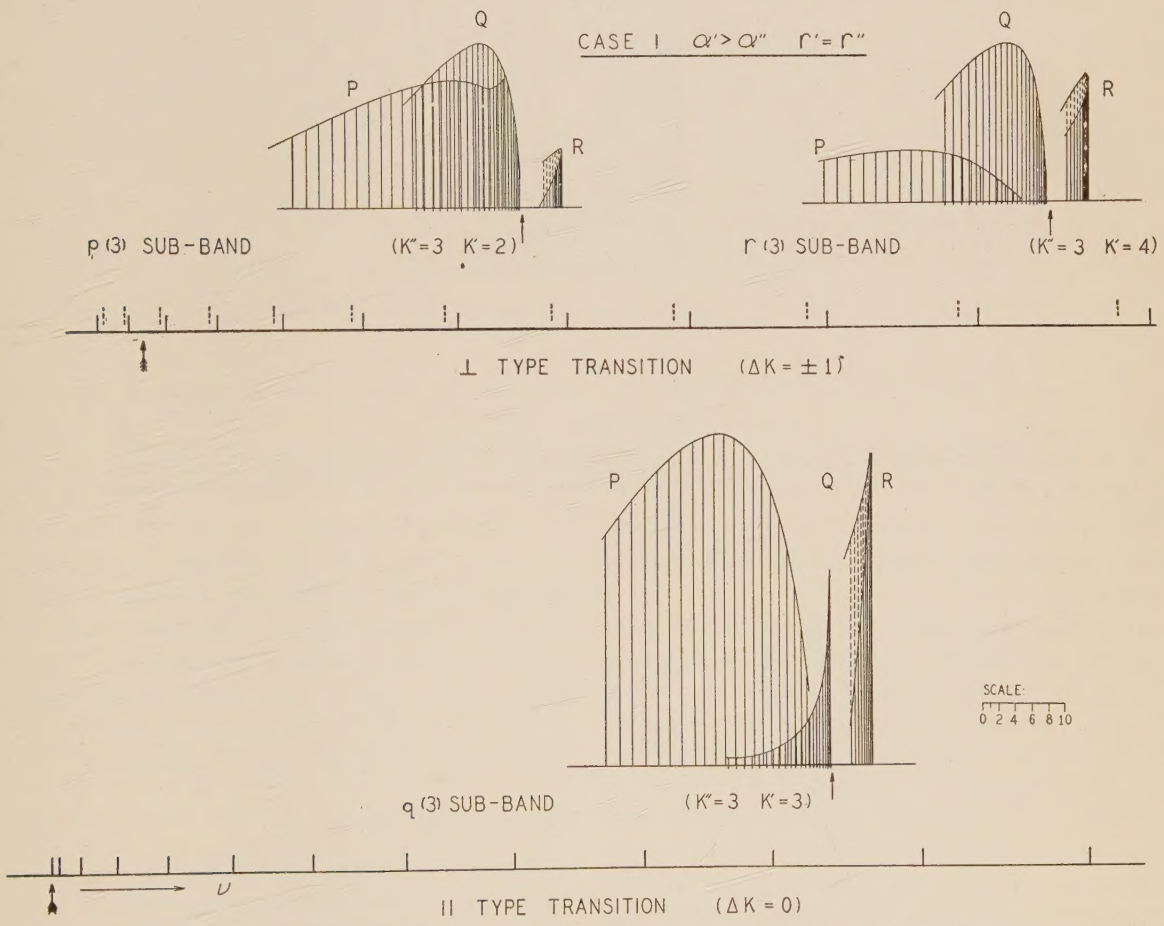

FIG. 3. Schematic representation of typical band structures of SO_2-like molecules, showing the "component parts" of both parallel- and perpendicular-type transitions when the only change in dimensions is (for absorption) an increase in the apex angle (case I). The K structure, which forms a set of origins for the sub-bands (J structure), is shown by lines of uniform height. Returning branches in the perpendicular-type K structures and in the J structures are shown by dashed lines. Lines of the Q branches are drawn below the axis. The feathered arrows correspond to origins of bands, unfeathered arrows to sub-band origins. The intensities correspond to a temperature of 200°K for the case of SO_2. For any other XY_2 molecule having the same ratio of moments of inertia I_b/I_c as SO_2, a change in scale combined with an appropriate temperature T' would yield an identical plot; T' is given by $T(I_b/I_b')$. Since $K'' = 3$ has been chosen for all three sub-bands exhibited here, the first lines in the P, Q and R branches shown are $P(3)$, $Q(3)$ and $R(3)$ where, as usual, the numbers in parentheses refer to J''. The J'' values run to 25.

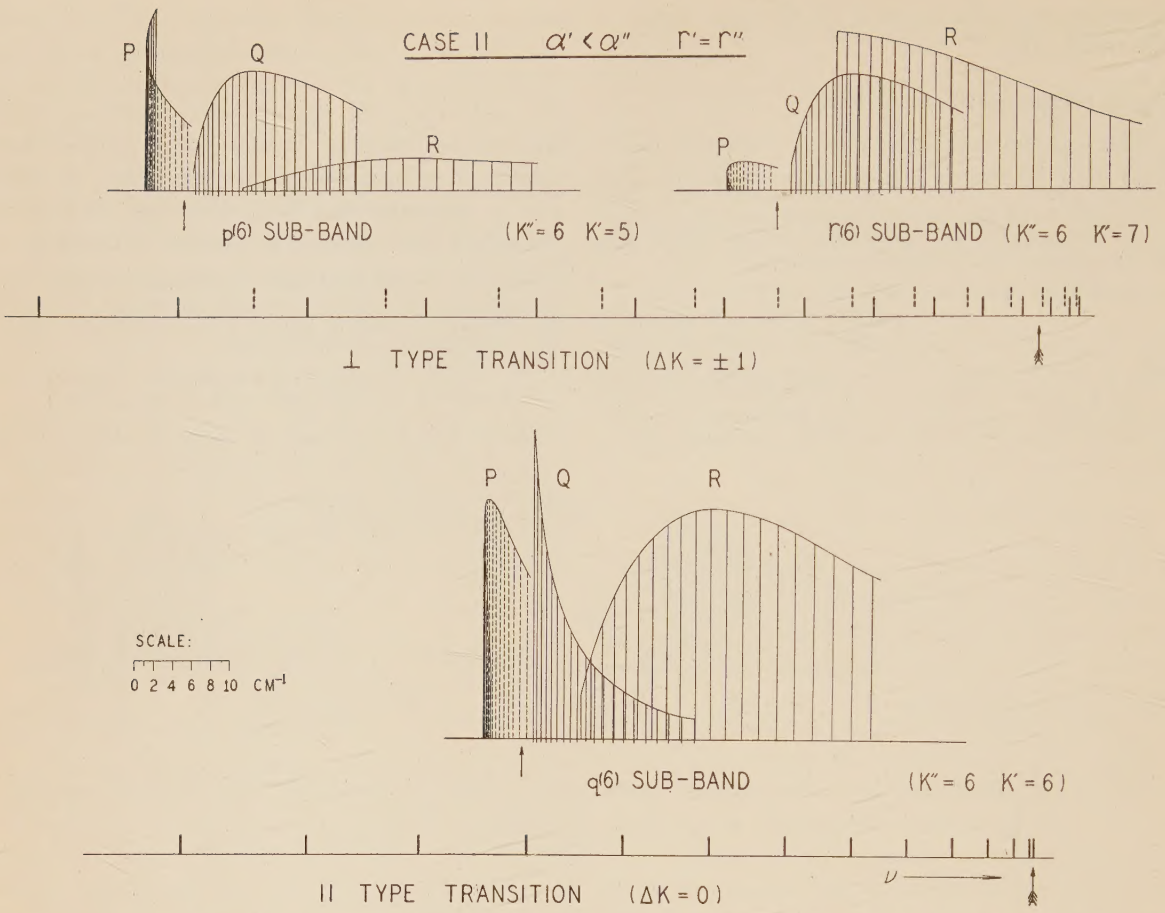

FIG. 4. Band structures for the case (in absorption) of a decrease in angle without change in bond distance (case II). In this instance the J and K structures degrade toward the ultraviolet and red respectively. See Fig. 3 for other details.

characteristic sharp edge, but will spread out on both sides.

In distinct contrast to the foregoing, cases III and IV will exhibit a shading of both J and K structures in the same direction; the whole band will possess a characteristic edge[8]—rather sharp in most instances—on the violet or red side according as $r' > r''$ or $r' < r''$.

The foregoing applies equally to parallel- and perpendicular-type transitions; in fact, it is only with some difficulty that one can expect to distinguish between these two types by observing the qualitative features of the bands. A returning branch of the K structure would distinguish a $\perp$ from a $\parallel$ type transition, the latter having no returning branch. However, the considerable overlapping should make it difficult to ascertain whether or not a returning branch of the K structure is present (cf. K structures of Figs. 3–6 where returning branches are shown by dashed lines); both $\perp$ and $\parallel$ types exhibit a convergence in the K structure. However, a plot of sub-band intensities should be of considerable aid.

[8] It may, of course, happen that the convergence in both structures is rather slow so that the intensity is small at the heads.

More general cases

The four cases just treated are, of course, very special; in general, both angle and bond distance change in going from one electronic state to another. In the preceding sections, the discussion of the coefficients was limited to a change in only one parameter (either α or r). To understand the effects of a change in both parameters, one considers first the effect of a change in one parameter, and using the results as a starting

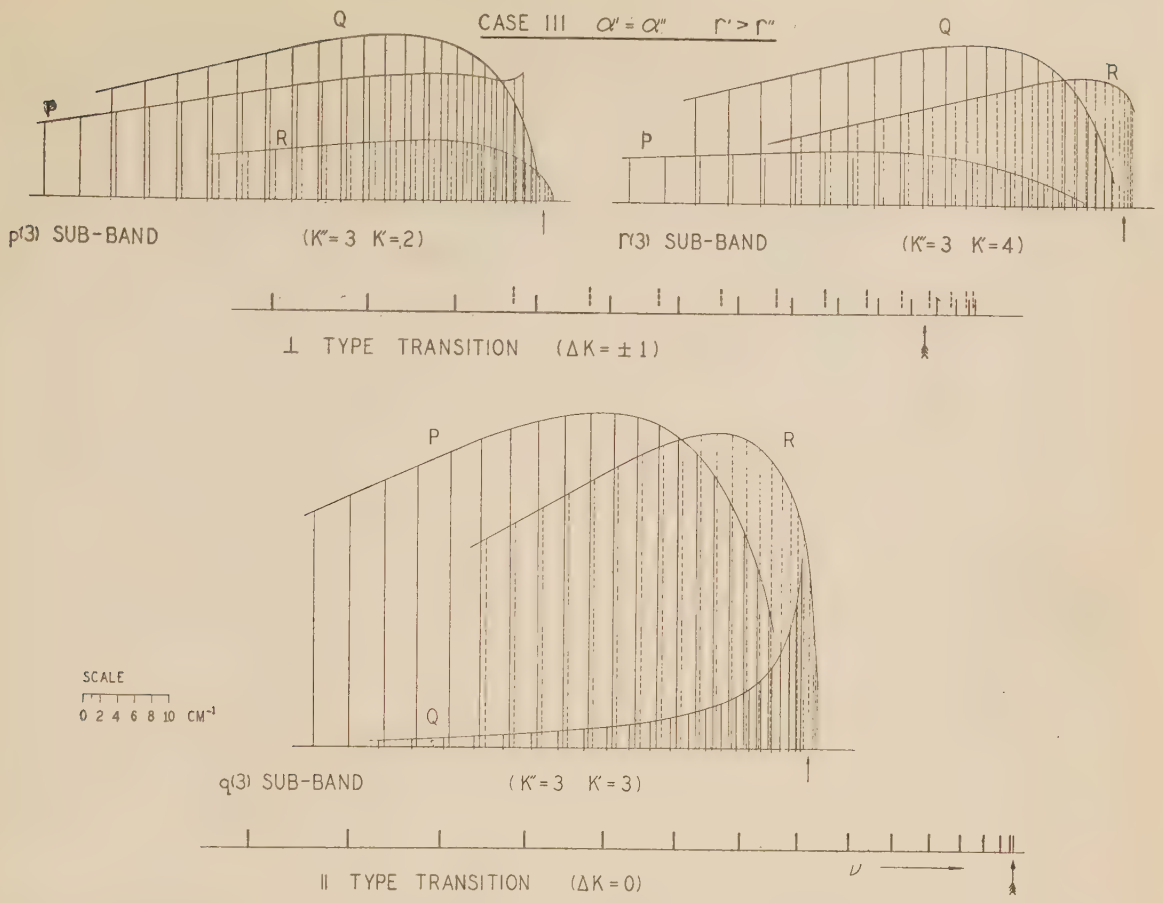

FIG. 5. Band structures for the case (in absorption) of an increase in bond distance without change in angle (case III). Note that both J and K structures degrade toward the red.

point, one may study the effect of a change in the second parameter.

From Fig. 2 one may obtain an insight into a variety of cases. As an example, let $\alpha'' = \alpha_2$, $r'' = r_2$ and $\alpha' = \alpha_1$, $r' = r_1$, and consider an absorption transition. B'' and C'' values are given by solid circles in Fig. 2, B' and C' by open circles. The effect of the decrease in angle alone (from α_2 to α_1) would be a movement along the solid curves from the solid circles to the open triangles. To obtain also the change in bond distance $r_2 \rightarrow r_1$, a shift is now necessary along the vertical at α_1 from the solid to the dashed curves, i.e., from the open triangles to the open circles. The net result is seen to be a considerable increase in B and a slight decrease in C for the example selected.

The fact that B and C change in opposite directions for a change in angle alone affords some interesting possibilities. In the example just given, $C' \approx C''$ resulted, yielding non-convergent K structure. This might suggest that $\alpha' \approx \alpha''$, $r' \approx r''$. However, inspection of the J structure, which (in our example) forms heads at relatively small quantum numbers, indicates $B' > B''$ definitely, since $-\Delta\alpha$, $-\Delta r$ both decrease B.

If the dimensions of the molecule should be practically unchanged in a transition, this fact would be immediately evident by the absence of heads in *both* J and K structures.

Typical Electronic Bands

Detailed diagrams of spectra of SO_2 and SO_2-like molecules have been worked out for each of the four special cases [Eqs. (6)] treated above, for values of J up to twenty-five and of K up to fifteen, for temperatures of 200° and of 300°K. Equations (1) and (2) were used to calculate the positions of lines, and the intensities were calcu-

lated from formulas taken from Dennison's review;[1] the frequency factor ν for absorption (or ν^4 for emission) was, however, omitted.

Since the oxygen nucleus has zero resultant spin, only one of the two possible levels associated with $|K|$ exists for $K>0$; for $K=0$, lines with alternate J values are missing.

Representative parts of the spectra of SO_2-like molecules for the four special cases are shown in Figs. 3–6. The ground state dimensions, $\alpha''=60°$, $r''=1.43$A, were taken to agree with electron diffraction values for SO_2;[9] for the excited states the following assumptions were made:

$$\begin{aligned} &\text{Case I.} && \alpha'=65°, && r'=r'', \\ &\text{II.} && \alpha'=55°, && r'=r'', \\ &\text{III.} && \alpha'=\alpha'', && r'=1.15r'', \\ &\text{IV.} && \alpha'=\alpha'', && r'=0.85r''. \end{aligned} \tag{7}$$

In each figure, the K (coarser) structure is shown for a parallel-type transition ($\Delta K=0$) and gives the origins of a set of sub-bands [cf. Eqs. (3)–(5)]; in addition, the structure of one sample sub-band is shown to the same scale. In each figure also, the K structure of a perpendicular-type transition ($\Delta K=\pm 1$) is similarly exhibited together with one sample sub-band from each of the two K branches (p and r). (A sub-band origin, shown by unfeathered arrow in the sample sub-band, should be brought into coincidence with the line representing each K transition.) It is, of course, necessary to make appropriate changes in relative intensity for the various sub-bands and to delete lines with $K>J$.

As a supplement to Figs. 3–6, Figs. 7 and 8 have been constructed to help in visualizing the change in intensity from one sub-band to the next. In the cases of both parallel- and perpendicular-type transitions, the intensity of the *most intense line* for each branch of the J structure has been plotted as a function of K. The dashed segments at $K=0$ have been inserted to remind one that the sub-bands having either K'' or K' equal to zero contain only half as many lines as other sub-bands, since lines with alternate J values are missing.

Returning to Figs. 3–6, one observes that in cases I and II, the J and K structures degrade in opposite directions, whereas in cases III and IV the two structures are shaded in the same direction; it is clear that the bands in the latter two

[9] V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. **62**, 1270 (1940).

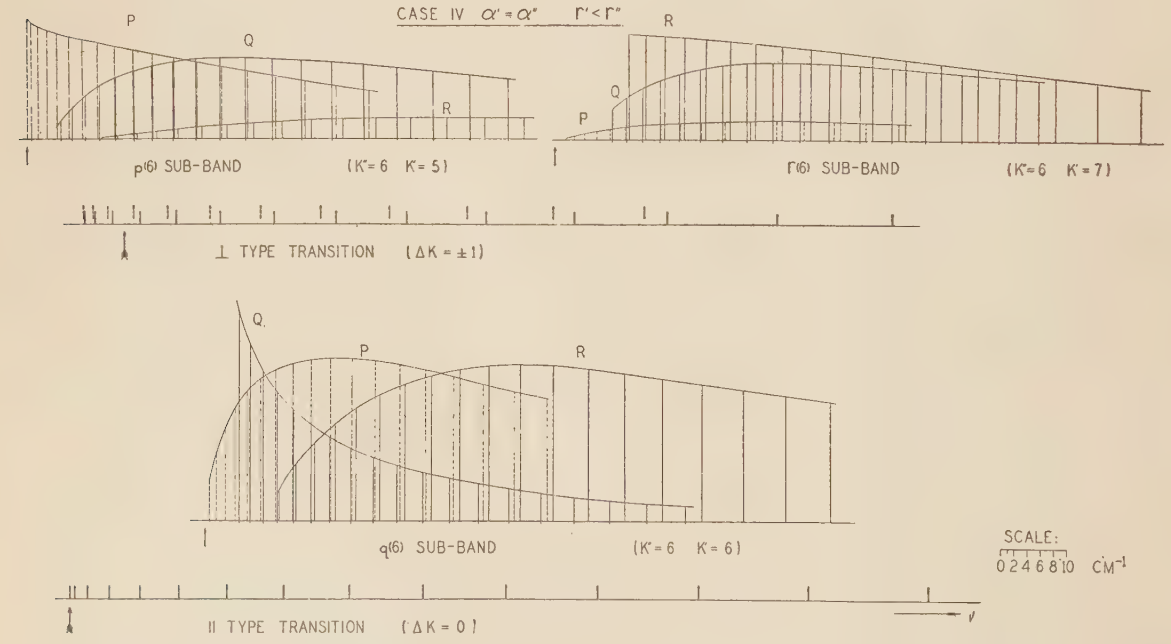

FIG. 6. Band structures typical of a decrease in bond distance without change in angle in an absorption transition (case IV). As in case III (Fig. (5)), J and K structures both degrade in the same direction, but here the direction is toward the ultraviolet.

cases must have a characteristic sharp edge.[8] In view of the considerable overlapping of the sub-bands and the usually large moments of inertia, the band may be so complicated that the only characteristic feature is the presence or absence of a sharp edge. However, even such meager information as the qualitative shape of the band envelope is valuable both for itself and as a help in the corresponding vibrational analysis; this latter point is discussed in the next section.

Application to Vibrational Analysis

In this last section the correlation of the qualitative characteristics of electronic bands with the intensity distribution in the associated vibrational structure is discussed. As a result of the interrelations that exist between rotational and vibrational structures, it is convenient to carry out the two analyses side by side. In the following, only absorption bands arising from the vibrationless level of the ground state will be considered. The fundamental frequencies of the normal state are usually known (mostly from infra-red and Raman work), so that transitions from excited vibrational levels in the ground state are easily recognized. However, in the event that these frequencies are not known, the temperature-sensitiveness of such bands makes them easy to pick out; or they can be made quite faint by lowering the temperature.

In making (or confirming) a vibrational analysis for an XY_2 molecule, two factors are to be considered: (1) the direction toward which the K structure (here the coarser) and the J (here the sub-band) structure degrade, (2) the intensity distribution in the vibrational structure. These two factors can be correlated by means of the Franck-Condon principle.

In the simplest instance there is one strong band, the vibrationless transition, accompanied by a few weaker ones. This intensity distribution is expected if the dimensions of the molecule are not appreciably changed in the transition to the excited state; the latter relation would be confirmed by slow convergence, if any, of both J and K structures.

If, on the other hand, there is one prominent series of quite evenly spaced bands, then by the Franck-Condon principle one may conclude that

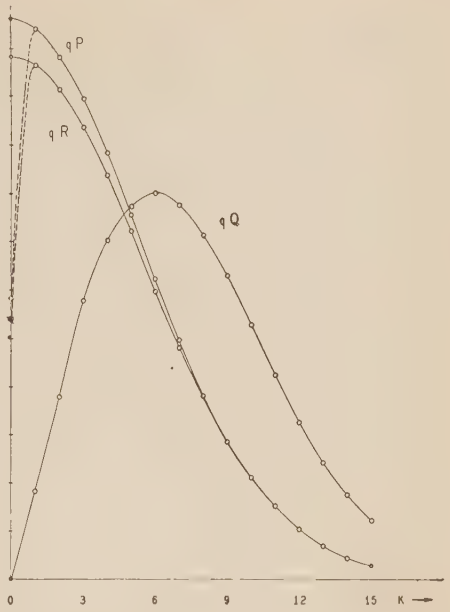

Fig. 7. The intensity of the strongest line of each branch (branches P, Q, R) of each sub-band is plotted as a function of K (i.e., K'') for a parallel-type transition, for SO_2 and SO_2-like molecules. The dashed segments from $K=1$ to $K=0$ are to remind one that only lines with alternate J values are present for $K=0$, so that the total intensity of each sub-band with $K=0$ is halved.

either the angle or bond distance has changed. If the bands exhibit a two-sided shading (cf. Figs. 3–4), it is primarily a change in angle that has occurred; but if both J and K structures degrade in the same direction so that the band as a whole possesses a sharp edge (cf. Figs. 5–6), then it is principally a change in bond distance that has taken place.

If the intensity distribution is more complicated, then the bond distance and angle must both have suffered appreciable changes, Δr (i.e., $r'-r''$) and $\Delta\alpha$ ($\alpha'-\alpha''$) in the electronic transition. Before attempting to discuss the interpretation of such cases with complicated intensity relations in terms of molecular changes, it is useful to consider first the converse problem of determining the directions toward which the J and K structures degrade for each of four possible types of transition in respect to the signs of the changes in r and α. For convenience let J and K with the subscripts $+$ or $-$ be used to denote whether the J or K rotational structure degrades toward the violet or the red. Referring to Table II, one observes that to each of the four types of changes in molecular dimensions (A, B, C, D)

there correspond two rotational-structure subtypes. In type A, the J structure is necessarily J_-; for, referring to Fig. 2, one observes that an increase in either α or r decreases B, hence certainly $B' < B''$. On the other hand, the K structure may be either K_+ or K_-, giving the two subtypes A_1 and A_2. This follows from the fact that an increase in α tends to increase C but an increase in r tends to decrease it; if the effect of the increase in r more than compensates that of the change in α, K is K_-; if not, then it is K_+. The discussion of the other types proceeds in similar fashion.

Returning to the original problem, one desires to determine the signs of the changes in molecular dimensions for a given type of band shading. Referring to Table III, one sees that for each of the K and J shading cases, there are two possible interpretations in terms of molecular changes. To ascertain which of the two possibilities is at hand, it would be necessary to determine which structure, J or K, converges more rapidly to form a head. This could be done easily if both structures are resolved. Usually the J structure is not completely resolved; however, the second differences in the J structure may be evaluated from resolved lines with high J values far from the head. From these evaluations, combined with a knowledge of B'', one can determine B'. Analogously, the second differences in the K structure can be determined, and finally C', since C'' is usually known. Hence the expressions

TABLE II. *Possibilities for shading of K and J structures for various* $\Delta\alpha$, Δr *types where* $\Delta\alpha$ *and* Δr *are changes in molecular dimensions.* ($\Delta\alpha = \alpha' - \alpha''$, $\Delta r = r' - r''$.) *The signs in column 3 indicate directions of shading* (+, *toward ultraviolet*, −, *toward red*).

			Band Shading	
Type	$\Delta\alpha$	Δr	K struc.	J struc.
A_1	+	+	+	−
A_2			−	−
B_1	−	−	−	+
B_2			+	+
C_1	+	−	+	−
C_2			+	+
D_1	−	+	−	+
D_2			−	−

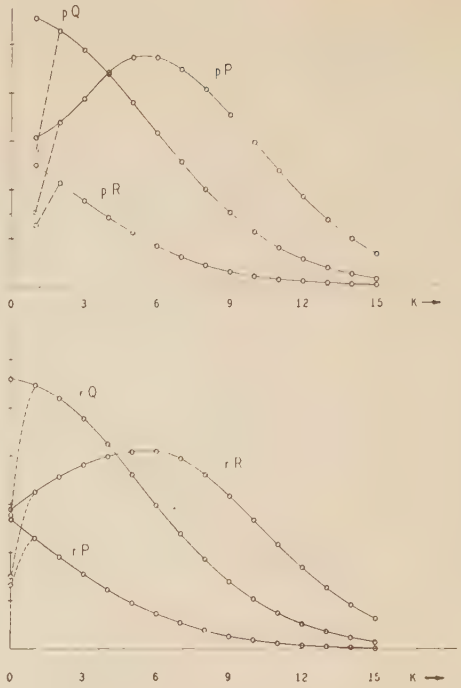

FIG. 8. Analogous to Fig. 7. Here a perpendicular-type transition is considered.

$|(B'-B'')/(B'+B'')|$ and $|(C'-C'')/(C'+C'')|$ can be evaluated. Their numerical values indicate the rate of convergence (or divergence) in the respective structures. A comparison of these serves as a criterion to distinguish between the two possibilities in Table III.

However, in practice it is usually not necessary to use this quantitative method because many spectra show such markedly dissimilar rates of divergence of the two structures that a mere inspection suffices. This situation occurs when both α and r change considerably. In the absence of marked differences, one has recourse to another criterion, taken from the vibrational intensity distribution. This situation arises from a change principally in only one of the two parameters, α and r (cf. p. 291).

As an example, suppose the spectrum observed is the case J_-K_-. Then definitely the bond distance has increased, but it remains to determine whether α has increased or decreased. If the J structure converges relatively more rapidly than the K, then $\alpha' > \alpha''$; if the opposite is observed, then $\alpha' < \alpha''$.

If one succeeds in determining the signs of the changes in dimensions, one is interested in know-

ing more explicitly how these changes are correlated with the vibrational intensity distribution. As yet, a quantitative treatment of the Franck-Condon principle for triatomic molecules is lacking, but some conclusions may be reached if simplifying assumptions are made.

Suppose, first, that the equilibrium bond distance increases by an amount Δr as a result of the electronic transition. Qualitative application of the Franck-Condon principle then shows that a pure v_1 vibrational progression should be developed (ν_1 = breathing frequency). Let us denote the quantum number of the strongest band in this series by $(v_1)_{max}$. Evidently $(v_1)_{max}$ is larger the larger is Δr.[10]

Again, suppose that $\Delta r = 0$ but that the equilibrium angle increases by an amount $\Delta\alpha$. In this event, a pure v_2 progression should be developed, whose strongest member may be designated by $(v_2)_{max}$ (ν_2 = deformation frequency). Finally, suppose both Δr and $\Delta\alpha$ differ from zero. Then both pure v_1 and pure v_2 progressions should be developed; and in addition mixed progressions. Further, for any given Δr value there is some corresponding $\Delta\alpha$ value such that $(v_1)_{max}$ and $(v_2)_{max}$ are equal.

If now a plane is defined by plotting $\Delta\alpha$ as ordinate against $\Delta r/r'$ as abscissa (it is found that $\Delta r/r'$ is more convenient for this purpose than Δr itself), then curves can be plotted in this plane passing through points where Δr and $\Delta\alpha$ are so related that $(v_1)_{max} = (v_2)_{max}$: see Fig. 9. If some simple assumptions are made,[10] it turns out that these curves are approximately straight lines passing through the origin (dashed lines in Fig. 9), given roughly by

$$\Delta\alpha = \pm 2\tfrac{1}{2}(\Delta r/r').$$

These lines evidently divide the plane into four regions, in two of which $(v_2)_{max} > (v_1)_{max}$ (dotted regions in Fig. 9), while in the other two $(v_1)_{max} > (v_2)_{max}$ (undotted regions in Fig. 9).

The $\Delta\alpha$, Δr plane can be divided into regions not only with respect to vibrational intensity distribution in the manner just discussed, but also with respect to rotational structure types. The rotational structure regions, like the vibrational distribution regions, are four in number. In the terminology introduced earlier, the four rotational regions may be labeled J_+K_+, J_+K_-, J_-K_+, and J_-K_-. The boundary between any two of these regions corresponds either to $B' = B''$ (J_+, J_- boundary) or to $C' = C''$ (K_+, K_- boundary). These boundaries can be located with the help of considerations used in plotting Fig. 2, and are given, for the case of absorption by SO_2 in its normal state, in Fig. 9.

TABLE III. *Interpretation of various K and J shading cases in terms of changes in molecular dimensions $\Delta\alpha$ and Δr.*

	Band Shading			
Case	*K* struc.	*J* struc.	$\Delta\alpha$	Δr
I	+	−	+	+
			+	−
II	−	+	−	−
			−	+
III	−	−	+	+
			−	+
IV	+	+	−	−
			+	−

Now then, if it is known which mode of vibration is more strongly excited and if the J, K shading can be determined, the possible changes in dimensions are limited to a region of the

[10] It is to be expected that for a given total intensity the number of bands in a v_1 progression (pure breathing series) is greater the larger the change in bond distance. If harmonic motion is assumed, one can estimate $(v_1)_{max}$, the quantum number of the strongest band in such a series. It turns out that $(v_1)_{max}$ is related to the frequency and the change in bond distance approximately according to

$$(v_1)_{max} = c(\Delta r)^2\nu_1. \qquad (a)$$

where ν_1 is the symmetrical valence or breathing frequency and c is a constant factor. It is interesting to observe that some deformation vibration is excited even though only the bond distance changes. If the angular change in a transition is $\Delta\alpha$, the distance of the Y atom in its normal state position, measured perpendicularly to the X−Y bond distance, from the excited state equilibrium position is approximately $\Delta s = r'\Delta\alpha$, where r' is the bond distance in the excited state. Then

$$(v_2)_{max} = c(\Delta s)^2\nu_2, \qquad (b)$$

where v_2 is the quantum number associated with ν_2, the deformation frequency, and c is the same as in Eq. (*a*). Empirically, $\nu_1 = 2\nu_2$ is found to be roughly true for the normal states of several XY_2 molecules. Hence from Eqs. (a) and (b)

$$(v_1)_{max} = (v_2)_{max} \qquad (c)$$

provided

$$(\Delta s) = \sqrt{2}(\Delta r).$$

In other words, Eq. (a) is true in case the change in α has the special value $\Delta_v\alpha$ given by

$$\Delta_v\alpha = \sqrt{2}(\Delta r)/r'. \qquad (d)$$

diagram where these properties overlap. For example, suppose the v_1 vibration is the stronger and the rotational structure is J_-K_-, then the possible changes in dimensions are represented by the area common to the vertically shaded region and the undotted region in the neighborhood of the positive $\Delta r/r'$ axis. At first it may appear that there still remains a considerable range of allowed changes in dimensions. However, a closer study should confine the region still more. For clearly, near the lower boundary (dashed line) of the region in the foregoing example, $(v_1)_{\max} \approx (v_2)_{\max}$. In addition, the J structure converges relatively slowly. For changes corresponding to points near the $\Delta r/r'$ axis, $(v_1)_{\max} > (v_2)_{\max}$ definitely, and both J and K structures degrade approximately at the same rate. Finally, in the vicinity of the upper boundary (solid line) the coarse K structure should degrade rather slowly, if at all.

A more favorable case occurs when the v_2 vibration is the more prominent and both J and K structures degrade in the same direction. In this instance, the overlapping regions are quite small.

If, for some molecule, the dotted region should coincide with the vertically-shaded region, one could determine from the J, K shading which vibration would be more prominent. Conversely, if the vibrational intensity were known, the J, K shading could be determined. Finally, from the figure the remarks made in connection with Tables II and III can be confirmed.

Some actual cases may be considered. Recent photographs of the absorption spectrum of ClO_2 taken on the 30-foot grating spectrograph by J. B. Coon in this laboratory[11] provide an interesting example to show the correlation between vibrational and rotational analysis. Here the structure is J_-K_- and both structures converge approximately at the same rate. On the basis of the present work it was seen that this indicates an increase in bond distance as the principal change in the transition and identifies the long series of some twenty bands as belonging to the breathing rather than the deformation frequency. The subsequent analysis proved this.

Photographs of the λ3880 system of SO_2 taken by Metropolis and Beutler[3] show quite other characteristics. Here the structure is J_-K_+. Of the two possibilities, case C_1 of Table II $(+\Delta\alpha, -\Delta r)$ is excluded because long progressions of the deformation frequency are not evident. Hence it must be case A_1 $(+\Delta\alpha, +\Delta r)$, and this is confirmed by the fact that the K structure converges more slowly than the J. That the changes are small is confirmed by the fact that the combination band having one quantum of each of the totally symmetrical vibrations is the strongest.

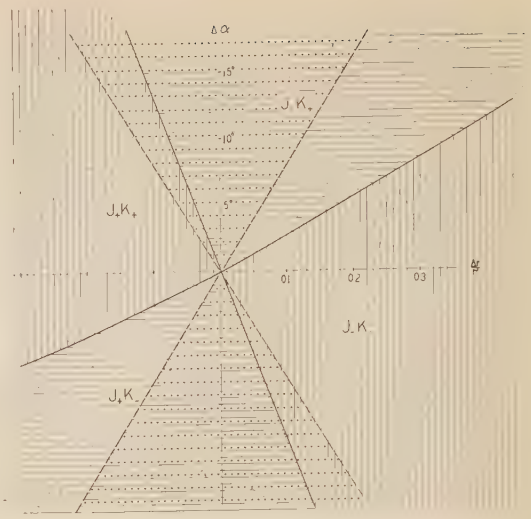

FIG. 9. A schematic diagram showing the directions of shading of the J and K structures for simultaneous changes in angle and in bond distance. As before, the subscripts indicate direction of shading (+, toward ultraviolet; −, toward red). Change in the value of the apex half-angle in degrees is plotted as ordinate, and $\Delta r/r'$ as abscissa, where $\Delta r = r' - r''$. The whole field is divided by two intersecting full heavy curved lines into four regions J_+K_+, J_-K_+, J_-K_-, J_+K_- indicated by horizontal or vertical hatching. The field is also divided in another way into four regions by two intersecting dashed lines: in the dotted region, the deformation is more prominent than the symmetrical valence vibration, whereas the opposite is true in the undotted region.

ACKNOWLEDGMENTS

The author is indebted to Professor Robert S. Mulliken, Dr. Hans G. Beutler and Dr. Wave H. Shaffer for their suggestions and encouragement and for many helpful discussions. Dr. Shaffer was also kind enough to help with the calculations of the intensity factors which were used for Figs. 3–6.

[11] J. B. Coon, Phys. Rev. **58**, 926(L) (1940).

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Vibrational Analysis of the Absorption System of Sulphur Dioxide at λ3400–2600

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Photographs of the bands of sulphur dioxide in the region of λ3400–2600 have been taken under low, medium and high dispersion, both at room temperature and at 200°K; the pressure of the absorbing gas was varied from 0.3 mm to 480 mm. Thirty bands can be represented by the formula

$$\nu = 29622 + 770v'_1 + 320v'_2 + 813v'_3 - 6v'^2_1 - 2.5v'^2_2 - 20v'_1v'_2 - 25v'_2v'_3 - 15v'_1v'_3,$$

where v'_1, v'_2, v'_3, are the quantum numbers of the symmetrical valence, the deformation and the antisymmetrical vibrations respectively. The three fundamental frequencies for infinitesimal vibrations in the upper electronic state are $\nu'_1 = 794$, $\nu'_2 = 345$ and $\nu'_3 = 833$ cm^{-1}. In addition, twelve bands have been identified that correspond to transitions from excited vibrational levels in the normal state. The relatively long v'_1 and v'_2 progressions indicate that both the bond distance and the angle have changed considerably in the transition to the excited electronic state. The vibrationless transition at 29622 cm^{-1} is weak, as one would have expected from considerations of the Franck-Condon principle. Substituting the three fundamental frequencies in the formula based on a valence force model, one obtains a value of 100° for the apex angle in the excited state, as compared with 120° in the normal state. The absence of any regularity in the rotational structure supports the resulting conclusion that the molecule in its upper state has become a more asymmetrical top.

Introduction

THE vibrational structure of the absorption bands of sulphur dioxide in the region λ3900–2600 has been studied in recent years by several investigators.[1–5] Previously Henri[6] had reported three main absorption regions in the near ultraviolet, (1) λ3900–3400, weak; (2) λ3370–2450, moderately strong; (3) λ2300–2000 and beyond, very strong. There was no evidence that these absorbing regions corresponded to three different electronic transitions except that the absorption intensities varied so widely. Watson and Parker[2] and Clements[4] investigated the absorption in regions (1) and (2) and concluded that both regions constitute one system; the bands at longer wave-lengths (λ3900–3400) were considered as transitions from excited vibrational states of the normal electronic state. Clements identified a moderately strong band at 31945 cm^{-1} as the band origin.

Retaining the assumption of a single upper electronic state, Samuel and Asundi[5] proposed two alternative analyses, the first a modification of the analysis of Clements, the second entirely new, with the vibrationless transition at 33303 cm^{-1}, one of the most intense bands. However, the proposals of Samuel and Asundi are not free from objections, as they themselves have remarked. In particular, their second analysis does not contain any bands with deformation vibration in the excited state. In addition, doubt is cast upon their assignment of the origin since there is no band at the position corresponding to the transition $(000)' \leftarrow (001)''$, although bands corresponding to higher vibrational levels of the normal state are assigned. Further comments on their analysis have been made by Price and Simpson.[7]

More recently, with the object of investigating the rotational band structure, the spectrum of sulphur dioxide has been photographed under low, medium and high dispersion in the region λ3900–2600 at various pressures from 0.3 mm to two atmospheres and at 800°, 300° and 200°K. As a result of this survey Metropolis and Beutler[8] established definitely that the electronic transition connected with the weak absorption around λ3800 is distinct from that associated with the stronger contiguous absorption toward shorter wave-lengths. Furthermore, even at pressures of a few millimeters and a dry ice temperature,

[1] A. K. Dutta, Acad. Sci. U. P. Bull. **1**, 89 (1931).
[2] W. W. Watson and A. E. Parker, Phys. Rev. **37**, 1484 (1931).
[3] A. Jonescu, Comptes rendus **197**, 35 (1933).
[4] J. H. Clements, Phys. Rev. **47**, 224 (1935).
[5] R. K. Asundi and R. Samuel, Proc. Ind. Acad. Sci. A2, 30 (1935).
[6] V. Henri, Nature **125**, 275 (1930).
[7] W. C. Price and D. M. Simpson, Proc. Roy. Soc. A165, 272 (1938).
[8] N. Metropolis and H. Beutler, Phys. Rev. **57**, 1078 (1940).

considerable structure was evident on the long wave-length side of the origin assigned by Clements (which is itself further toward the red than the origin assumed by Samuel and Asundi). This latter fact suggested that the origin must lie at still longer wave-lengths. Finally, the large number of bands excited indicated that the dimensions of the molecule have changed considerably in the electronic transition, so from considerations based on the Franck-Condon principle, one would expect the vibrationless transition to be quite weak.

In view of the foregoing, it was thought advisable to reconsider the vibrational structure of the system around λ3200; the results obtained form the basis of the present work.

Experimental

Sulphur dioxide obtained commercially was distilled twice before being admitted to a reservoir. The Pyrex absorption tube was 4.5 cm in diameter and 1 m in length with flanges at each end. Cylindrical quartz cells of the same diameter as the absorption tube and of 2-cm length with two quartz windows as bases were sealed onto the flanges with Picein. When these cells were evacuated, no water vapor condensed on the windows at low temperatures. From one end of the absorption tube, a side arm was connected to a mercury diffusion pump. At the other, the following were connected in series: stopcock *A*, a small cell whose volume was very nearly 15.9 cc (1/100 the volume of the absorption tube), stopcock *B*, a vertical U-tube, and finally a reservoir.

The U-tube was surrounded by a dry ice-acetone bath. At the equilibrium temperature of CO_2-acetone, the pressure of SO_2 is 8 mm. To obtain pressures less than 8 mm, the small cell was filled with SO_2 at 8 mm pressure, stopcock *A* being kept closed. Then stopcock *B* was closed and *A* opened, allowing the gas to expand into the absorption tube. Thus one could obtain any desired pressure between 0.008 mm and 8.0 mm simply by repeating the operation the required number of times. For higher pressures, crushed dry ice was slowly added to acetone in a thermos flask and sufficiently agitated to obtain a uniform temperature. The absorption tube was then filled at the temperature corresponding to the desired pressure. A pentane thermometer was used (sufficiently accurate here). Finally, a

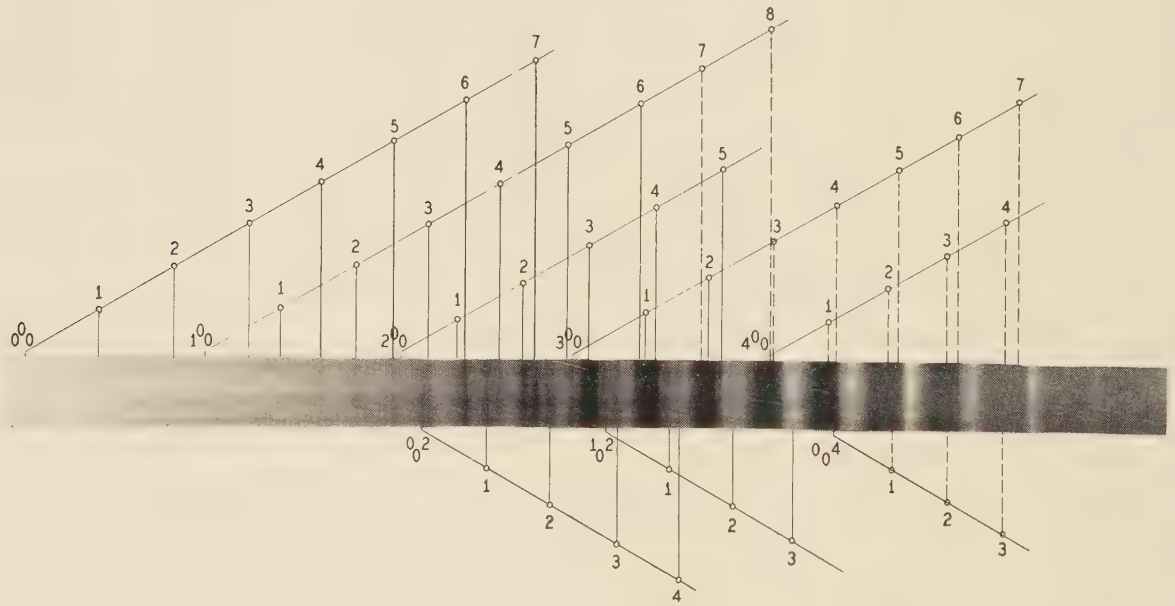

Fig. 1. Spectrogram of SO_2 at 5 mm pressure and 200°K in the region λ3400–2900, taken on the Hilger E1 spectrograph. The vibrational analysis is indicated at the sides of the spectrum; the quantum numbers v'_1, v'_2, v'_3, correspond to the symmetrical valence, the deformation, and the antisymmetrical vibrations respectively. The running numbers are for v'_2. The positions of bands near the system origin have been taken from spectrograms of SO_2 made at higher pressures. The dashed lines correspond to bands calculated by Eq. (1), which is based on bands marked by solid lines.

thermally insulated metal trough, which could be packed with dry ice, surrounded the absorption tube.

For studying the gross features of the electronic system, photographs were taken with a Hilger E3 spectrograph having a dispersion of 15.8A/mm at λ3200 and a Hilger E1 having a dispersion of 5.2A/mm in the same region. The light source used for these photographs was a conventional hydrogen discharge tube carrying 0.8 ampere at 5000 volts. In addition, it was desirable to have photographs taken on the 30-foot grating spectrograph to guide and confirm the vibrational analysis (cf. later discussion and preceding paper[9]). For this purpose a high power tungsten light source[10] was used. For the low dispersion photographs, the exposure time was about three minutes; for medium dispersion, exposures ranged from twenty minutes to an hour. In the region of λ3100 the high dispersion photographs required twenty hours with a slit width of twelve microns. In some cases where it was desired to observe the shape of the band envelopes, the maximum resolving power of 300,000 in the second order of the grating spectrograph was not necessary, and a wide slit of forty microns was used. The high dispersion photographs then required only three hours. Process and Eastman 33 plates were used. An iron arc provided the comparison spectrum.

Description and Analysis of Spectrum

A series of exposures taken under low dispersion at various increasing pressures of SO_2 exhibits a maximum absorption intensity around λ2900 with gradual fading out on both sides. (A photograph of a similar set of SO_2 exposures has been published by Watson and Parker.[2]) As the pressure is increased, the region of marked absorption increases toward both longer and shorter wave-lengths; at atmospheric pressure of SO_2, the long wave-length limit is nearly λ3400. The weaker electronic band system at longer wave-lengths appears at about 50 mm and is well developed at 760 mm. The latter system is more or less clearly separated from the strong absorption region under investigation.

From a study of the vibrational intensity distribution, one may conclude that both apex angle and bond distance have changed considerably in the transition. Consequently, from considerations based on the Franck-Condon principle, the vibrationless transition should be weak. Thus the system origin must lie at longer wave-lengths than the relatively strong bands identified by previous investigators as the vibrationless transition, that is, greater than λ3125. That it does is indeed confirmed by a comparison of spectrograms taken on the Hilger E1 spectrograph at pressures of 0.8 mm, 1.6 mm and 5.0 mm both at room temperature and at dry ice-acetone equilibrium temperature. They show conclusively that the bands lying at wave-lengths longer than λ3125 are definitely *not* from excited vibrational levels but from the vibrationless level in the normal state. The Boltzmann factor for one quantum of the deformation vibration is about 3.5 times smaller at 200° than at 300°K, for two quanta the ratio is 12.25; for one quantum of the ν_1 frequency the ratio is about 15.5. No such changes in intensity were observed for the bands mentioned when the temperature was lowered from 300° to 200°K.

At first it was suspected that the band corresponding to the vibrationless transition, although weak, would be among the bands that appear on the spectrogram taken with 5.0 mm pressure of SO_2 at 200°K. The band of longest wave-length under these conditions is at 30685 cm^{-1}. From this band a progression of quite evenly spaced bands proceeds toward higher frequencies at intervals of approximately 300 cm^{-1}, a spacing which is to be identified with the deformation, or bending, frequency. In addition to the latter progression, another progression, starting approximately in the middle of the first interval of the first progression, proceeds toward shorter wave-lengths with the same intervals. The obvious conclusion is that these two progressions differ by one quantum of the symmetrical valence, or breathing, frequency, and that the origin lies at still longer wave-lengths.

The relative positions of the two progressions indicate that the symmetrical valence frequency ν'_1 is some odd multiple of one-half the deformation frequency ν'_2. It is easily seen that a value near 450 cm^{-1} for ν'_1 is incompatible with the

[9] N. Metropolis, Phys. Rev. **60**, 283 (1941).
[10] H. Beutler and N. Metropolis, J. Opt. Soc. Am. **30**, 115 (1940).

TABLE I. *Absorption bands of sulphur dioxide. Observed bands and their associated vibrational quantum numbers. The bands without letters or * arising from the vibrationless level of the normal state have been used to determine the coefficients in Eq. (1). The intensity values are those of Clements. In the last column, the mean effective heights of the lower state vibrational levels above the vibrationless level are given as determined by Clements using a temperature variation method. The differences between observed and calculated bands are also given. The calculated values are from Eqs. (1) and (2). All data are for maxima of observed bands. The frequencies of bands labeled with letters or marked with * are taken from Clements, all others are from new measurements. Brackets on left of quantum numbers indicate overlapping bands. Brackets on right indicate that the intensity is to be divided between them. Intensity values in Parentheses are estimated by the author.*

ν	$v'_1v'_2v'_3$	$v''_1v''_2v''_3$	I†	Temp. Variation (cm^{-1})	Obs. ν − Calc. ν
29439	0 1 0	0 1 0	0.3	200	24
29622	0 0 0	0 0 0	0.3		0
29648	1 1 0	0 2 0	0.5		15
29742	0 2 0	0 1 0	0.8		18
29940	0 1 0	0 0 0	1.4	0	0
29994	2 0 0	1 0 0	1.2	1000	−12
30048	0 3 0	0 1 0	1.2	1000	18
	0 7 0	1 1 0			−16
30175	1 1 0	0 1 0	(1.2)		16
30249	0 2 0	0 0 0	3	150	0
30280	2 1 0	1 0 0			20
30386	1 0 0	0 0 0	6	300	0
	0 6 0	0 2 0			− 7
30435	0 0 1	0 0 0	(1.5)		− 3
30465	1 2 0	0 1 0	(3.0)		15
30551	0 3 0	0 0 0	10	70	− 4
30685	1 1 0	0 0 0	15	50	1
30721	0 1 1	0 0 0	20	0	− 6
30760	1 3 0	0 1 0	(10)		22
30848	0 4 0	0 0 0	25	60	− 8
30980	1 2 0	0 0 0	40	40	4
31037	1 4 0	0 1 0	40	40	17
31125	2 0 0	0 0 0	40	0	−10
31140	0 5 0	0 0 0			−12
31258	0 0 2	0 0 0	(30)		10
31275	1 3 0	0 0 0	(30)		12
31405	2 1 0	0 0 0			− 8
31430	0 6 0	0 0 0	60	500	−13
	2 3 0	0 1 0			− 3
31520	0 1 2	0 0 0	65		4
31567	1 4 0		60		22
31675	2 2 0		120		−10
31717	0 7 0		100		−21
31778	0 2 2		80		0
31840	1 5 0		90		16
31855	3 0 0				−14
31940	2 3 0			0	−13
31991	1 0 2		(20)	0	3
32033	0 3 2		(25)	0	− 3
32119	1 6 0		(30)	0	24
32140	3 1 0		(40)	0	9
32198	2 4 0	0 0 0		0	−17
32235	1 1 2		(25)	0	0
32276	0 4 2		(15)	0	−12
32377*C*	1 7 0		600	0	15
	3 2 0				− 6
32438	2 5 0		(120)	0	−34
32479	1 2 2		(15)	0	1
32607*D*	1 8 0		600	0	−18
	3 3 0				−21
	4 0 0				7
32713	1 3 2		(5)	0	− 3
32850*E*	3 4 0		1200	0	−23
	4 1 0				12
	0 0 4				−18
33080*F*	3 5 0		1700	0	−30
	4 2 0				10
	0 1 4				− 6
33313*G*	3 6 0		2000	0	−30
	4 3 0				15
	5 0 0				− 3
	0 2 4				15
33547*H*	3 7 0		1900	0	−23
	4 4 0				27
	5 1 0				13
	0 3 4				15
33760*J*	3 8 0		2000	0	−33
	4 5 0				22
	5 2 0				14
33960*K*	4 6 0		1700	0	10
	5 3 0				6
34030*L*	3 9 0		1600	0	20
	6 0 0				7
34241*	6 1 0[1]		700	0	20
34180*M*	4 7 0[1]		1600	0	22
	5 4 0[1]				24
34396*N*	6 2 0[1]		1600	0	7
34620*O*	6 3 0[1]		1700	0	19
34724*	7 0 0[1]		200	0	3
34785*	6 4 0[1]		1000	0	2
34970*	6 5 0[1]		500	0	9

† Intensity values from Clements (presumably at room temperature).
[1] Possibilities for superposed bands have not been exhausted.

experimental findings. For instance, it is difficult to explain the absence of many bands in case that $\nu'_1 = 450$ cm^{-1} is assumed. In addition, other considerations make this value unlikely. Using 750 cm^{-1} for ν'_1, however, one can identify not only a v'_1 progression but also combination overtones in harmony with the vibrational intensity distribution. Finally, the extrapolated pure v'_1 and pure v'_2 progressions have a common point at 29622 cm^{-1}, which must then be the origin of the band system. The photographs taken at higher pressures of SO_2 confirmed the positions of the origin and of the bands that were too weak on the low pressure photographs.

A band at 31258 cm^{-1} is moderately strong and comparable in intensity to its immediate neighbors. This band cannot be fitted into the scheme of the symmetrical vibrations, and temperature variation data of Clements[4] indicate that it is not from excited levels in the normal

state. Assuming that this band corresponds to two quanta of the antisymmetrical frequency ν'_3, one can also explain eight additional bands as combinations of the symmetrical vibrations with two quanta of the antisymmetrical. In addition, a very weak band is found at 30432 cm^{-1}, corresponding to one quantum of the ν'_3 frequency. Although this transition is forbidden by electronic selection rules,[11] it may, nevertheless, be permitted by vibronic selection rules.[12] In a later section, we shall discuss the possibilities for the electronic character of the upper state.

Figure 1 is a reproduction of a spectrogram taken at 200°K and at 5 mm pressure of SO_2, marked with a schematic representation of the vibrational analysis. Bands from excited vibrational levels of the normal state are not labeled in this photograph.

Table I contains a list of the bands according to increasing wave number, with their vibrational quantum number assignments. The wave numbers of the bands labeled A, B, C, $\cdots$ and of those marked with * are taken from the work of Clements, together with their absorption intensities. However, from only the present measurements, it is found that the vibrational energy levels of the excited state can be represented by the formula

$$\nu = 29622 + 770v'_1 + 320v'_2 + 813v'_3 - 6v'^2_1 - 2.5v'^2_2 - 20v'_1v'_2 - 25v'_2v'_3 - 15v'_1v'_3, \quad (1)$$

where v'_1, v'_2, v'_3 are the symmetrical valence, deformation, and antisymmetrical vibrational quantum numbers respectively. The three fundamental frequencies for the normal state as determined from Raman and infra-red data[13] are

$$\nu''_1 = 1152 \text{ cm}^{-1}, \quad \nu''_2 = 525, \quad \nu''_3 = 1361. \quad (2)$$

In order to account for the prominent series called A, B, C, $\cdots$ by Clements, Eq. (1) plus the term $+0.15v'^3_1$ have been used to calculate higher members of several progressions, and the results are indicated in Fig. 2 by dashed lines. Thus it is possible to explain the strong progression of Clements, not as a simple v'_2 progression as he did, but by superpositions of various higher combination bands. By application of the Franck-Condon principle, one expects that the pure v'_1 and v'_2 progressions, although of considerable length, do not contain the most intense bands. The latter are found among the combination overtones. Thus the individual bands have already considerable intensity and their superposition effects even higher absorption intensities.

Table I also contains a comparison of the observed and calculated positions of the bands. In the region where the overlapping of intense bands creates a fortuitous appearance of a simple progression, no attempt has been made to identify the various superposed bands individually; instead, the values of the observed maxima are taken from Clements. Better agreement between observed and calculated values cannot be expected for the following reasons: (1) The position of the maximum intensity is used since the location of the band origin is not known; (2) no account is made of resonance

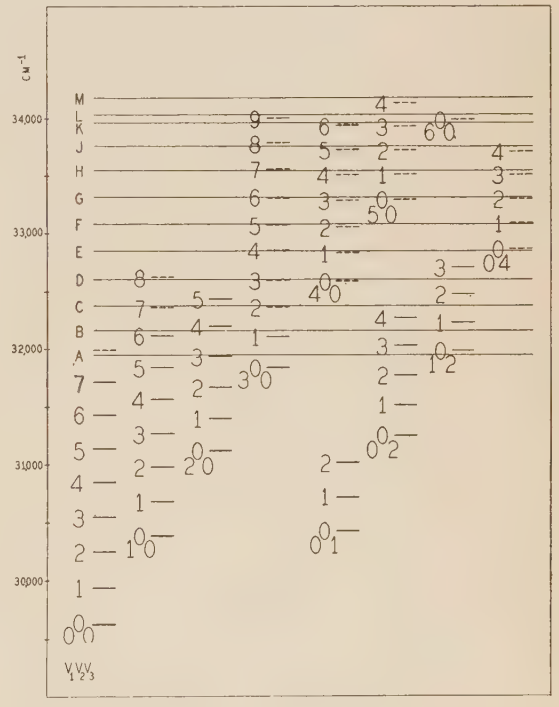

FIG. 2. Vibrational term scheme of the upper electronic state. The bands represented by short solid lines have been used to evaluate the coefficients in Eq. (1). The dashed lines correspond to bands calculated by this equation. Thus the A, B, C, $\cdots$ absorption regions can be interpreted as superpositions of several bands rather than as a pure v'_2 progression.

[11] G. Herzberg and E. Teller, Zeits. f. physik. Chemie **B21**, 410 (1938).
[12] Cf. R. S. Mulliken, Phys. Rev. **59**, 873 (1941).
[13] Cf. H. Sponer, *Molekülstruktur* (Julius Springer, Berlin, 1934).

interactions between superposed vibrational levels; (3) overlapping bands arising from low lying excited vibrational levels of the ground state may distort the intensity distribution of a given band appreciably.

Included in Table I are eleven bands which arise from excited levels of the normal state and whose positions are in agreement with what may be calculated from Eq. (1) combined with Eqs. (2).

It was hoped that the photographs taken under high dispersion would exhibit some characteristic feature in the rotational structure, as does the system at λ3880, so that analogous positions in each band could be measured and used instead of the intensity maxima under low dispersion. Unfortunately this was not the case.

Discussion of Results

When the values of the three upper state fundamental frequencies, $\nu'_1 = 794$ cm^{-1}, $\nu'_2 = 345$ cm^{-1}, $\nu'_3 = 833$ cm^{-1}, are substituted in theoretical formulas based on a valence force model,[14] one obtains two solutions, 100.3° and 79.7°, as possible values for the apex angle. Since there are only seven members of appreciable intensity in the pure v'_2 progression, one is strongly inclined to favor the value of 100.3°.[15] Jonescu[16] from a study of rotational structures in the region λ3000, using the first and second orders of a twenty-one foot grating spectrograph (resolving power not given), reports in a brief communication an apex angle of 96° in the excited and 120° in the normal state. He calculated and plotted band structures assuming various values for α, but keeping the assumed bond distance always fixed at $r = 1.36$A for both electronic states, and compared the results with observed structures. Because, however, of the considerable superposition of bands shown by the present work to exist in the region Jonescu studied, it is very doubtful that any single band can be present there under favorable conditions for investigating the rotational structure; furthermore, calculation shows that the most intense lines for room temperature must be around $J = 20$. Consequently Jonescu's results do not appear to be conclusive, even though there is good agreement of his α' with the value calculated from the fundamental frequencies obtained here.

That the angle has decreased in the upper state is, however, confirmed by the present high dispersion photographs, where the irregular band structures indicate quite definitely that the molecule becomes a more asymmetrical top (see below). The type of structure which would have been expected if the angle had remained unchanged or increased slightly in the transition can be judged from a study of the high dispersion photographs of the λ3880 system of SO_2 and of the figures of the preceding paper.

Clements developed a temperature variation method for determining the heights of initial vibration levels above the vibrationless level. The determination is based on photometric measurements of absorption at two temperatures not too widely separated. The method was first applied to SO_2, and it is interesting to see whether his results are in harmony with the present analysis. Since the various contiguous regions of the spectrum, in which he applied the method, did not overlap, it was possible only for him to compare bands in each region with reference to a fiducial band in that region. However, the present analysis shows that the fiducial bands for all the regions are from the vibrationless level of the normal state. Thus it is possible to compare various regions directly. Referring to the last column of Table I, one sees that the present assignments are in harmony with Clements' data, except, perhaps, for the value of 200 cm^{-1} for $(010)' \leftarrow (010)''$, which lies on the long wave-length side of the vibrationless transition. Very likely, however, an absorption band (arising from the vibrationless level) of the adjacent electronic system overlaps $(010)' \leftarrow (010)''$, giving effectively a value of 200 cm^{-1}.

The considerable overlapping in the absorption regions A, B, C, $\cdots$ may explain why Kusch and Loomis[17] obtained such widely varying magnetic rotation spectra for these "bands."

[14] C. R. Bailey and A. B. D. Cassie, Proc. Roy. Soc. **A137**, 630 (1932).

[15] Cf. J. B. Coon, Phys. Rev. **58**, 926(L) (1940). He reported only two bands in a v'_2 progression in ClO_2 corresponding to a change in apex angle from 122° to 114°.

[16] A. Jonescu, Comptes rendus **196**, 1476 (1933).

[17] P. Kusch and F. W. Loomis, Phys. Rev. **55**, 850 (1939).

The electronic character of the excited state is indicated as singlet by the strong absorption intensity. The presence of two bands in which definitely one quantum of the antisymmetrical vibration is excited, taken in connection with a consideration of the vibronic selection rules, show that the excited state must be either $^1A_1$ or $^1B_2$ (cf. reference 12, Table XI). Were it possible to determine whether the bands under discussion are of the perpendicular or parallel type, one could determine uniquely the nature of the upper electronic state ($^1B_2$ if these bands are of the parallel type, $^1A_1$ if they are perpendicular).

In conclusion, a few remarks may be made concerning the prospects of a rotational analysis of this system. As a result of a decrease in the apex angle ($2\alpha' = 100°$) in the transition, the regularity of symmetric top levels must be entirely lost (cf. Fig. 4 of reference 12), thus rendering the analysis more difficult. In addition, there should be greater overlapping of sub-band structure. Another point is the scarcity of bands free from overlapping; those bands which are intense enough at low pressures, where low temperatures could then be used to reduce the complexity, are considerably overlapped, as we have seen. Those near the system origin require higher pressures to obtain sufficient absorption. The increased pressure precludes work at low temperatures, tends to broaden the rotational lines and makes probable the presence of overlapping, low lying excited vibrational levels of the normal state.

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